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(54) Wear resistant solid film lubricants, their preparation and use.

(57) Surfaces which have substantially continuous frictional contact, eg. reciprocating engine parts, are coated with a solid film lubricant having excellent wear characteristics and adhesion. The parts in question may be pistons, and the area to which the wear resistant solid lubricant film is bonded is the piston skirt -- i.e., all or a portion of the area below the piston rings. The lubricant is composed of a polyimide derived from 2,2-bis[4-(4-amino-phenoxy)phenyl]hexafluoropropane ("4-BDAF") and an aromatic tetracarboxylic acid (or dianhydride or ester thereof) containing fluorinated carbon.

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Description**WEAR RESISTANT SOLID FILM LUBRICANTS, THEIR PREPARATION AND USE**

This invention relates to a wear resistant solid film lubricants which can be used on surfaces for engine parts, notably reciprocating pistons.

5 It has been proposed heretofore to use as a coating for air bearings a film of fluorinated carbon embedded in a polyimide of 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane ("4-BDAF") and pyromellitic dianhydride ("PMDA"). In air bearings the rotating surfaces operate with a film of air between them and only occasionally do the metal surfaces come in actual contact with each other. Heretofore this coating composition has been indicated to be suitable for other, unspecified purposes.

10 It has also been proposed heretofore to utilize as a protective coating for piston skirts a system composed of graphite embedded in 4-BDAF/PMDA polyimide or in the polyimide of 4-BDAF and BTDA (benzophenonetetracarboxylic acid dianhydride). While this coating was reasonably effective (it survived for about 400 hours in engine dynamometer tests), a coating lasting at least 1,000 hours in this test is desired.

15 In accordance with a preferred aspect of this invention, reciprocating engine parts which involve substantially continuous frictional contact are coated with a solid film lubricant having excellent wear characteristics and adhesion. The parts in question are usually pistons, and the area to which the wear resistant solid lubricant film is bonded is the piston skirt — i.e., all or a portion of the area below the piston rings.

20 In general, the lubricant film of the invention is composed of a polyimide of 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane ("4-BDAF") and an aromatic tetracarboxylic acid (or dianhydride or ester thereof) containing fluorinated carbon, usually containing from 25 to 125 parts by weight of fluorinated carbon per 100 parts by weight of the polyimide resin ("phr"), and preferably about 30 to about 100 phr of the fluorinated carbon.

25 The invention also includes a general process for producing a wear resistant solid film lubricant for surfaces which are generally in frictional contact, which process comprises forming on at least one of said surfaces a matrix of a polyimide derived from 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane and an aromatic tetracarboxylic acid, a dianhydride or ester thereof, containing fluorinated carbon.

30 To form the solid lubricant film on a piston it is desirable to apply to the piston skirt surface a dispersion of the fluorinated carbon in a solution of a polyamic acid of 4-BDAF and the aromatic tetracarboxylic acid (or dianhydride or ester thereof) and subject the wetted surface to a temperature sufficient to drive off the solvent.

35 This process may be repeated for a sufficient number of times to build up a coating of desired thickness. Thereupon sufficient heat is applied to cure the coating (i.e., convert the polyamic acid polymer into polyimide Polymer). For best results the dispersion should be applied by means of spraying apparatus using a suitably dilute solution of the polyamic acid containing the dispersed finely divided or powdery fluorinated carbon.

40 The aromatic tetracarboxylic acid utilized in the coatings of this invention includes pyromellitic acid, 3,3',4,4'-benzophenonetetracarboxylic acid, 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane, oxydiphtalic acid, and biphenyl tetracarboxylic acid. In most cases, these acids are employed in the form of their dianhydrides although they may be employed as diesters or as the free acids or as mixtures of such materials. Use of pyromellitic acid and benzophenonetetracarboxylic acid (or their dianhydrides or esters) acid is preferred. As is well known the polyamic acids are formed by reacting essentially equimolar quantities of 4-BDAF and the aromatic tetracarboxylic acid (or dianhydride or ester thereof) in a suitable solvent.

45 Any of a variety of solvents may be used to form the solution of the polyamic acid. For this purpose dipolar aprotic solvents such as dimethylformamide, dimethylacetamide, N-methyl-pyrrolidone, diglyme, dimethylsulfoxide, or the like are preferred. Other solvents which may be used include ethers such as tetrahydrofuran and tetrahydropyran; chlorohydrocarbons such as methylene dichloride; ketones such as acetone and methyl ethyl ketone; alcohols such as methanol, ethanol, propanol and isopropanol; and the like.

50 Various grades of fluorinated carbon are available as articles of commerce from Allied-Signal Corporation under the trademark ACCUFLUOR. A particularly useful grade is ACCUFLUOR 1030 which is recommended by Allied-Signal for applications where good wear resistance is desired.

The filled coatings of the invention are extremely adherent to metals and alloys used in the manufacture of pistons, such as aluminum. Moreover, the solid film lubricant adheres tenaciously to the metal substrate despite the exposure of the coating during use to lubricating oils which usually contain various additives such as dispersant-detergents, viscosity index improvers, rust inhibitors, and the like.

55 The following example illustrates the practice of this invention.

EXAMPLE

60 Fluorinated carbon (ACCUFLUOR 1030) was dispersed in solutions of 4-BDAF/PMDA polyamic acid and 4-BDAF/BTDA polyamic acid. The resultant compositions were spray coated on aluminum piston skirts. The dispersions were formed at two different concentration levels (15 and 35 percent pigment volume concentration or 25 and 50 weight percent based on total solids) in each of the two polyamic acid systems.

Thus four different spray formulations were produced and employed.

The compositions of the spray formulations were as follows:

Formulation 1 - based on an initial solution containing 12.5 g of 4-BDAF/PMDA polyamic acid for each 37.5 g of N-methyl-pyrrolidone (NMP) solvent.

50 g initial solution

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8.9 g NMP

168.4 g methyl ethyl ketone (MEK)

4.2 g fluorinated carbon

This formulation had a pigment volume concentration of 15 percent.

Formulation 2 - same as Formulation 1 except it contained 12.5 g of fluorinated carbon. Thus Formulation 2 had a pigment volume concentration of 35 percent.

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Formulation 3 - same as Formulation 1 except it was based on an initial solution containing 12.5 g of 4-BDAF/BTDA polyamic acid for each 37.5 g of NMP solvent. Thus this formulation had a pigment volume concentration of 15 percent.

Formulation 4 - same as Formulation 3 except it contained 12.5 g of fluorinated carbon. Thus Formulation 4 had a pigment volume concentration of 35 percent.

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In preparing these spray formulations the initial solution of polyamic acid in NMP was first diluted with all of the additional NMP and 40 percent of the amount of MEK to be used in forming the diluted spray solution. Another 40 percent of the MEK to be used in forming the spray solution was used as the dispersion medium for the fluorinated carbon which was dispersed therein by means of a high shear stirrer. This dispersion was promptly mixed with the polymer solution. The remaining 20 percent of the MEK to be used in forming the spray solution was then used to rinse the shear stirrer and these washings were combined with the rest of the spray formulation. The formulation was continuously stirred using a magnetic stir plate.

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Aluminum pistons to be coated with the foregoing formulations were scrubbed with a detergent powder, rinsed thoroughly with tap water, sanded with 400-grit paper to remove imperfections and rinsed with tap water and dried with towels. Thereupon the cleansed pistons were solvent rinsed and wiped with dry toluene followed by solvent rinsing and wiping with dry acetone. Finally, the so-treated pistons were heated for two hours at 315°C when prepared for use with the 4-BDAF/BTDA polyamic acid formulations or 357°C when prepared for use with the 4-BDAF/PMDA polyamic acid formulations.

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The dried and cleansed pistons were spray coated on a turntable using a commercially available spray gun operated at a pressure of 275 kPa nitrogen (anhydrous). The piston ring areas and other areas to be devoid of coating were covered by means of adhesive tape. The spraying procedure was as follows:

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1. Preheat piston to 107°C in an oven.
2. Remove piston from oven and allow to cool to 65°C.
3. Spray coat with formulation at room temperature to form an approximately 13 micrometer coating after solvent removal.
4. Oven dry at 107°C for 15 minutes.
5. Repeat Steps 2-4 to produce another 13 micrometer layer.
6. Increase oven temperature to 240°C and hold the piston at this temperature for 1 hour.
7. Cool piston to 107°C.
8. Repeat Steps 2-7 until desired coating thickness is obtained.
9. Cure coating on the piston in the oven for 2 hours at 240°C.
10. Raise oven temperature to post-cure temperature of 315°C for the formulations based on 4-BDAF/BTDA, 357°C for the formulations based on 4-BDAF/PMDA. Hold the coated piston at this temperature for 2 hours.
11. Slowly cool the piston to room temperature.

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The thickness of the coatings on the finished coated pistons were as follows:

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<u>Number of Coats Applied</u>	<u>Pigment Volume</u>	<u>Coating Thickness</u>	50
2	15	31.7-50.8 micrometers	
2	35	50.8-69.9 micrometers	55
4	15	82.5-88.9 micrometers	
3	35	82.5-88.9 micrometers	60

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The coated pistons are suitable for use in the operation of the internal combustion engine for which they are adapted. The coating adheres tenaciously during the operation and the coating exhibits improved lubricity as

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compared to the base metal.

5 **Claims**

10 1. The use of a matrix of a polyimide derived from 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane and an aromatic tetracarboxylic acid, a dianhydride or ester thereof, and containing therein fluorinated carbon as a wear resistant lubricant for surfaces which are in substantial continuous frictional contact.

15 2. The use of Claim 1 wherein the fluorinated carbon is present at from 25 to 125, preferably about 30 to about 100, parts by weight per 100 parts by weight of polyimide.

20 3. The use of Claim 1 or Claim 2 wherein the polyimide is derived from at least one of the following aromatic tetracarboxylic acids or a dianhydride or ester thereof:

25 pyromellitic acid

benzophenonetetracarboxylic acid

2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane

oxydiphtalic acid

biphenyltetracarboxylic acid.

30 4. A piston having bonded to its skirt portion a wear resistant solid film lubricant consisting essentially of fluorinated carbon in a matrix of a polyimide derived from 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane and at least one of the following aromatic tetracarboxylic acids or a dianhydride or ester thereof:

35 pyromellitic acid

benzophenonetetracarboxylic acid

2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane

oxydiphtalic acid

biphenyltetracarboxylic acid.

40 5. An engine comprising at least one cylinder having a piston reciprocatably disposed therein and means for applying liquid lubricating oil to surfaces of each such cylinder and piston, each such piston having bonded to its skirt portion a wear resistant solid film lubricant consisting essentially of fluorinated carbon in a matrix of a polyimide derived from 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane and at least one of the following aromatic tetracarboxylic acids or a dianhydride or ester thereof:

45 pyromellitic acid

benzophenonetetracarboxylic acid

2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane

oxydiphtalic acid

biphenyltetracarboxylic acid.

50 6. A process for producing a coated piston which includes applying to the skirt portion thereof a coating consisting essentially of a dispersion of fluorinated carbon in a solution of a polyamic acid of 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane and at least one of the following aromatic tetracarboxylic acids or a dianhydride or ester thereof:

55 pyromellitic acid

benzophenonetetracarboxylic acid

2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane

oxydiphtalic acid

biphenyltetracarboxylic acid.

60 7. The use of any one of Claims 1 to 3, an engine as claimed in Claim 5, or a process as claimed in Claim 6, wherein the aromatic tetracarboxylic acid component of the polyamic acid is based on pyromellitic acid or its dianhydride or an ester thereof.

65 8. The use of any one of Claims 1 to 3, an engine as claimed in Claim 5, or a process as claimed in Claim 6, wherein the aromatic tetracarboxylic acid component of the polyamic acid is based on benzophenonetetracarboxylic acid or its dianhydride or an ester thereof.

70 9. A process for producing a wear resistant solid film lubricant for surfaces which are generally in frictional contact, which process comprises forming on at least one of said surfaces a matrix of a polyimide derived from 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane and an aromatic tetracaboxylic acid, a dianhydride or ester thereof, containing fluorinated carbon.

75 10. A process as claimed in Claim 9 further defined by the specific feature(s) of any one of Claims 2, 3, 7 or 8.



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(54) Wear resistant solid film lubricants, their preparation and use.

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DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	CHEMICAL ABSTRACTS, vol. 93, no. 4, July 1980, page 141, abstract no. 28865e, Columbus, Ohio, US; R.L. FUSARO: "Effect of thermal aging on the tribological properties of polyimide films and polyimide bonded graphite fluoride films", & LUBR. ENG. 1980, 36(3), 143-53 * Abstract *	1-3	C 10 M 111/04 // (C 10 M 111/04 C 10 M 103:02 C 10 M 107:44) C 10 N 30:06 C 10 N 40:00 C 10 N 50:02 C 10 N 50:08 C 10 N 60:08
Y	IDEM	4-8, 9, 10	
X, Y	---	1-3	
Y	FR-A-2 530 263 (CENTRAL GLASS) * Page 1, line 33 - page 2, line 6; page 5, line 26 - page 6, line 16; page 10, lines 22-32 * ---	1-10	
Y	EP-A-0 133 533 (HITACHI LTD) * Page 3, line 15 - page 4, line 14; page 12, lines 9-24; page 13, lines 15-16; page 14, lines 16-24; page 16, line 6 - page 17, line 18; page 27, examples 26-28 *	4-8	TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
Y	PATENT ABSTRACTS OF JAPAN, vol. 11, no. 262 (C-442)[2709], 25th August 1987; & JP-A-62 63 628 (HONDA MOTOR CO., LTD) 20-03-1987 * Abstract *	1-10	C 10 M C 08 L
A	GB-A-1 088 728 (E.I. DU PONT DE NEMOURS) * Page 1, line 10 - page 3, line 36; page 5, lines 68-76; page 8, lines 6-85 * -----	4-8	
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	01-02-1989	HILGENGA K.J.	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			